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First-Principles Study of Adsorption of Dimethyl Methylphosphonate on the TiO$_2$ Anatase (001) Surface: Formation of a Stable Titanyl (Ti=O) Site

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ABSTRACT: Ab initio calculations have been performed to model the molecular adsorption of dimethyl methylphosphonate (DMMP) on the (001) surface of the anatase form of TiO$_2$. Both the relaxed unreconstructed (1 × 1)- and the (4 × 1)-reconstructed clean surfaces have been analyzed. Adsorption occurs via a Ti—O=P dative bond to a coordinatively unsaturated surface Ti site. In both cases, one of the two Ti—O—Ti bridge bonds at the Ti adsorption site breaks leading to the formation of a stable Ti=O titanyl group. This species has not been reported in previous studies of adsorption on TiO$_2$ surfaces but is seen, in the present work, as an intermediate in the dissociative adsorption of H$_2$O.
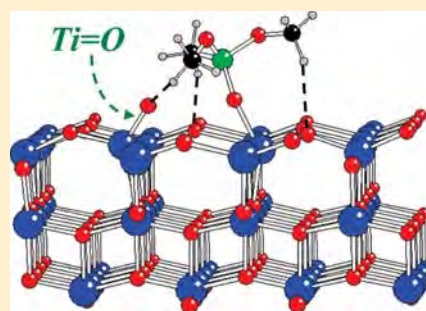
1. INTRODUCTION

One of the many applications[1,2] for titanium dioxide (TiO$_2$) is in the catalytic or photocatalytic destruction, through oxidation, of toxic chemicals. One important class of such species consists of organic reagents containing a P=O group, which constitute hazards to the environment and to personnel.[3] Many of these are much too dangerous for routine experimentation; hence, relatively nontoxic simulants are used instead, the most significant of which is (CH$_3$)(CH$_3$O)$_2$P=O (dimethyl methylphosphonate, DMMP).

Due to the importance of this topic, there is a substantial amount of literature[4−25] dealing with the interaction of DMMP with TiO$_2$, either in the dark or during photoexcitation of the TiO$_2$ to generate electron−hole pairs. Recent studies[26,27] have also investigated the photocatalytic decomposition of actual toxic compounds on TiO$_2$. On an OH-free rutile (110) surface in ultrahigh vacuum (UHV), DMMP adsorption is molecular at room temperature[5−7] and occurs via a Ti---O=P dative bond at a 5-fold-coordinated Ti$_{5c}$ site. Figure 1 shows a model[25] for the corresponding structure on anatase (101) and also identifies the T$_{5c}$, Ti$_{6c}$, and O$_{2c}$ sites. The Ti$_{6c}$ is 6-fold coordinated, and the O$_{2c}$ is a 2-fold-coordinated O atom bridging Ti$_{5c}$ and Ti$_{6c}$ sites. For a given Ti$_{5c}$ site, adjacent O$_{2c}$ sites can be labeled as "nearest" (N) or "next-nearest" (NN) as illustrated in Figure 1. In addition to the dative bond, C—H---O$_{2c}$ bonds form as indicated, based on the CH---O distances and C—H---O bond angles, and have been analyzed[25] using the Atoms In Molecules (AIM) theory.

In contrast to the UHV experimental data, computational results for DMMP on OH-free rutile (110) and anatase (101) and (100) surfaces[24,25] find that dissociation is energetically favored over molecular adsorption. It is noted here that the anatase (100) and (010) surfaces are isostructural, as are the (101) and (011) surfaces. For anatase (101), molecular

adsorption is exothermic with an energy of ΔE_{ads} = −19.1 kcal/mol as obtained in a two-dimensionally periodic slab (2-DPS) calculation;[25] whereas, ΔE_{ads} = −25.0 kcal/mol is found for a possible first step in dissociation. Similar results for molecular vs. dissociative adsorption are found for the OH-free rutile (110) and anatase (100) surfaces.

Most of the experimental work in this area involves infrared spectroscopy and high-surface-area (HSA) powders for which anatase, rather than rutile, is usually the major constituent.[28] Furthermore, the (101) face, which is the most stable surface for a bulk single crystal of anatase, makes only a small contribution to these powders. Here the (100) (or equivalently (010)) and (001) surfaces are dominant. In virtually all cases, the HSA powders are at least partially hydroxylated, and molecular adsorption on OH-terminated HSA TiO$_2$ can be seen only below ~214 K (refs 17 and 18). Above this temperature, reaction with OH occurs easily; although, DMMP does not react with liquid H$_2$O under normal conditions.[29]

The fact that experiment shows predominantly molecular adsorption on OH-free rutile (110) but dissociative adsorption on hydroxylated HSA powders, together with the computational result that dissociation is energetically favored on OH-free surfaces, suggests that dissociation is kinetically limited in the absence of surface OH. It has been proposed[8,9,11,18] that OH groups promote the first step in the reaction through nucleophilic attack on the P atom by the hydroxyl O atom, leading to formation of a P(−O−)$_2$ bridge between Ti sites and either an adsorbed CH$_3$O group or free CH$_3$OH. Successive steps lead eventually to a tenacious PO$_x$ residue that poisons further

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14. ABSTRACT

Ab initio calculations have been performed to model the molecular adsorption of dimethyl methylphosphonate (DMMP) on the (001) surface of the anatase form of TiO2. Both the relaxed unreconstructed (1 1)- and the (4 1)- reconstructed clean surfaces have been analyzed. Adsorption occurs via a Ti?OdP dative bond to a coordinatively unsaturated surface Ti site. In both cases, one of the two Ti-O-Ti bridge bonds at the Ti adsorption site breaks leading to the formation of a stable TidO titanyl group. This species has not been reported in previous studies of adsorption on TiO2 surfaces but is seen, in the present work, as an intermediate in the dissociative adsorption of H2O.

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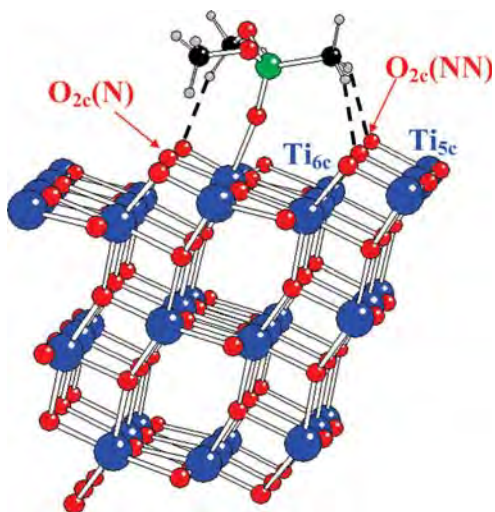**Standard Form 298 (Rev. 8-98)**
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Figure 1. Geometry-optimized structure (from ref 25) for DMMP adsorbed on the anatase (101) surface. The dashed lines indicate C—H---O bonds, and different Ti and O sites are labeled. The atom colors are blue (Ti), red (O), green (P), black (C), and gray (H).

catalytic activity. A recent study[30] of the adsorption of $(CH_3)(OH)_2P=O$ (methylphosphonic acid, MPA) on OH-free rutile TiO_2 (110) combining scanning tunneling microscopy in UHV and ab initio computation found that dissociation to form a $(CH_3)P(=O)(-O-Ti_{5c})_2$ bridge and two OH sites occurs spontaneously at room temperature. However, such a process may be less likely for DMMP, in which the two OH groups of MPA are replaced by CH_3O.

The purpose of the present work is to investigate the adsorption of DMMP on the OH-free anatase (001) surface that, together with the anatase (100), is the major constituent in most HSA TiO_2 powders. This is a necessary preliminary to achieving an understanding of the effects of OH on the adsorption and dissociation of DMMP on different TiO_2 surfaces. The (001) surface is also known to exhibit a high degree of photocatalytic activity.[31] It will be seen that molecular adsorption of DMMP on anatase (001) is distinctly different from that on other TiO_2 surfaces. On the relaxed but unreconstructed (001)-(1 × 1), as well as on the more stable (4 × 1)-reconstructed surface, adsorption of DMMP leads to an extensive rearrangement of surface atoms not seen for other TiO_2 surfaces.

2. COMPUTATIONAL DETAILS

All calculations were based on 2-DPS models and employed the *CRYSTAL 06* and *09* codes,[32,33] which use Bloch functions constructed from localized Gaussian basis sets. Most of the relevant details are given elsewhere[24,25] in connection with the anatase (101) and (100) surfaces. For the (001) surface, a slab was formed from a (4 × 4) supercell with a thickness of 4 O—Ti—O trilayers, giving a total of 12 atomic layers and 64 TiO_2 units per supercell. A slab of this thickness is sufficient for convergence of the (001) surface structure and energy[34,35] and has been used in previous studies[36–39] of adsorption on anatase (001). The need for a large supercell will become apparent when the adsorption of DMMP is discussed. DMMP was placed only on the upper surface with one molecule per supercell, giving a coverage of one DMMP per 16 Ti_{5c} surface sites. The initial

DMMP conformation was the one identified[40,41] as the lowest in energy for the gas-phase molecule.

Two different computational approaches were employed in order to verify the lack of a significant influence on the final results. In the first, relaxation was done at the restricted Hartree—Fock (RHF) level, followed by a total-energy calculation using density functional theory (DFT). In the second, the entire calculation was performed using DFT. In both cases, DFT employed the B3LYP functional, the applicability of which to studies of the adsorption of organic species on TiO_2 has been discussed elsewhere.[42] During relaxation, the atoms in the lowermost O—Ti—O trilayer were frozen in the optimized bulk-lattice positions obtained previously[25] while all other TiO_2 and DMMP atoms were unconstrained. Geometry optimizations used an effective-core pseudopotential for Ti and a modified 6-31G(d) basis set for O, as previously described.[24,25] The DFT energy calculations for the relaxed structures used the all-electron basis sets for Ti and lattice O, also as previously described.[24,25] The 6-31G(d,p) basis sets appropriate to the free molecule were used for DMMP since larger molecular basis sets led to linear-dependency problems in 2-DPS calculations.[24,25] Due to the large supercell size, all calculations used a (1 × 1) Monkhorst-Pack grid. Other computational parameters including the convergence criteria for geometry optimization, the definition of adsorption energy (ΔE_{ads}) and the correction for basis set superposition error (BSSE) are described elsewhere.[24,25] The basic approach outlined above was tested in several ways as described in the following two sections.

3. RESULTS

3.1. Adsorption on the (1 × 1) Surface. The ideally terminated (001) surface (Figure 2a) is nonpolar and stoichiometric, with one O_{2c} and one O_{3c} for every Ti_{5c}. It is also autocompensated since the excess electron density on the Ti_{5c} is transferred to the electron-deficient O_{2c} to give a closed-shell configuration on both. However, recent results[43] show that relaxation is not complete on the (001)-(1 × 1) surface and that there are occupied surface states in the band gap very close to the valence band maximum (VBM). An alternative termination, in which the O_{2c} layer is removed to give a surface consisting of Ti_{3c} and O_{3c} sites, is neither stoichiometric nor autocompensated and is expected to be much less stable.

Table 1 shows the structural changes resulting from relaxation. These consist largely of displacements of O atoms in the first and second O—Ti—O trilayers in opposite directions along the [100] axis, together with an outward displacement of O_{2c} atoms ("O1" in Table 1) along the surface normal.[35,43,44] The Ti_{5c} atoms ("Ti1" in Table 1) also undergo displacements opposite to those of O_{2c}, resulting in short and long Ti_{5c}—O_{2c} bonds. As is seen in Table 1, displacements beyond the first Ti and third O layers are very small; however, the displacements in the outermost layers lead to a large tensile stress, which is relieved by the (4 × 1) reconstruction,[45] described in Sec. 3.3, or by adsorption.[36,46]

Figure 2b shows the starting structure for molecular adsorption of DMMP on the relaxed (1 × 1) surface. It has previously been shown[24,25] that Ti---O=P bonding at a coordinatively unsaturated Ti site is the most favorable mechanism for adsorption and that bonding to a methoxy O atom is negligible. Previous work[25] also shows the formation of C—H---O_{2c} hydrogen bonds and analyzes these using the AIM theory. Examination of Figure 2b shows that initial structures differing by a rotation of

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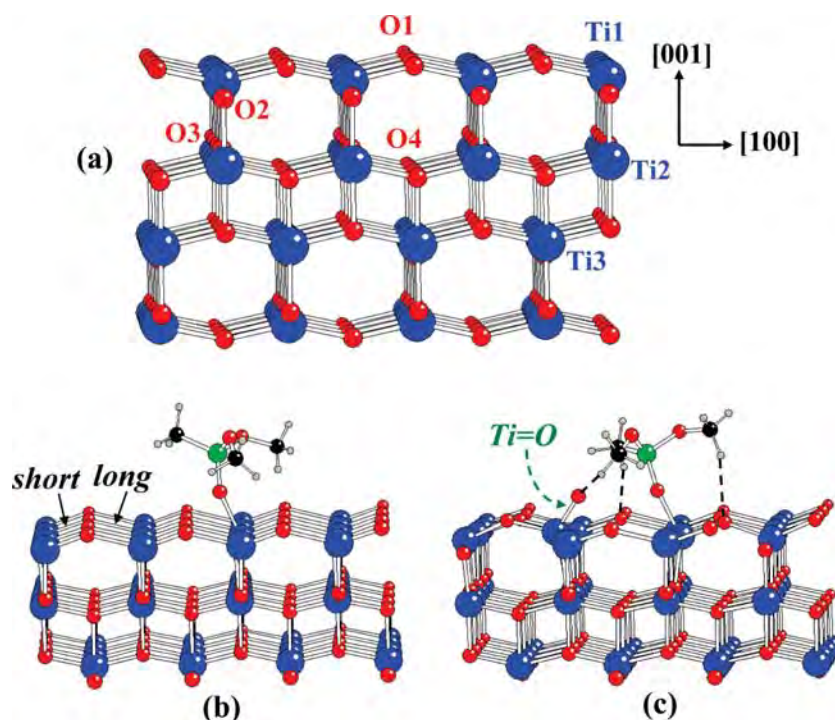dx.doi.org/10.1021/jp200009s |*J. Phys. Chem. C* 2011, 115, 6741–6747

Figure 2. (a) The ideally terminated anatase (001) surface. The outermost Ti (O) atoms are 5-fold (2-fold) coordinated, and the Ti and O sites referred to in Table 1 are labeled. (b) The relaxed (001) surface with adsorbed molecular DMMP before further relaxation. "Short" and "long" Ti_{5c}—O_{2c} bonds (cf. Table 1) are labeled. (c) Same as (b) but after relaxation following adsorption of DMMP. The Ti=O site is labeled, and the dashed lines indicate possible H-bonds identified on the basis of the CH---O distances (2.22 to 2.55 Å) and C—H---O bond angles (139° to 162°).

Table 1. Comparison of Calculated Atomic Displacements Due to Relaxation of the Anatase (001)-(1 × 1) Surface[a]

atom	this work[b]	this work[c]	ref 35[d]	ref 44[e]
O1	−0.14; +0.06	−0.17; +0.06	−0.19; +0.08	−0.09; +0.02
O2	−0.10; −0.03	−0.16; −0.01	−0.17; −0.02	−0.07; 0.00
O3	+0.07; −0.03	+0.10; −0.04	+0.11; +0.01	+0.05; +0.01
O4	+0.01; −0.02	+0.01; 0.00	+0.02; 0.00	−0.01; +0.01
Ti1	+0.10; −0.08	+0.07; −0.09	+0.04; −0.06	+0.05; −0.04
Ti2	−0.01; −0.02	−0.03; −0.01	−0.01; +0.01	0.00; +0.01
Ti3	0.00; −0.03	0.00; −0.02	+0.02; 0.00	
Ti1—O1 short[f]	1.745	1.738	1.76	
Ti1—O1 long[f]	2.195	2.207	2.20	
∠(Ti1—O1—Ti1)[g]	147.2°	146.7°	146°	

[a] All distances are in Ångstroms. The first (second) number gives the displacement along the [100] ([001]) direction. All displacements along [010] are zero. See Figure 2 for definitions of atoms and axes. O1 is a 2-fold-coordinated O_{2c} atom. All other O atoms are 3-fold-coordinated O_{3c} sites. Similarly, Ti1 is a Ti_{5c}, while all other Ti atoms are Ti_{6c}. [b] Optimization using RHF with ECPs. [c] Optimization using DFT with the B3LYP functional and ECPs. [d] DFT plane-wave/pseudopotential calculation; 6 O—Ti—O trilayers; PBE functional. [e] DFT calculation; Bloch functions constructed from localized Gaussian basis sets; 10 O—Ti—O trilayers; B3LYP functional. [f] These values refer to the "short" and "long" Ti_{5c}—O_{2c} bond lengths. The ideally terminated value is 1.936 Å in the present work. [g] This is the bond angle at the surface O_{2c} site. The ideally terminated value is 155.2° in the present work.

~90° about the P=O bond are inequivalent due to the presence of short and long Ti_{5c}-O_{2c} bonds. The various structures differ as to whether C—H---O_{2c} bonds form to short- or long-bonded O_{2c} atoms. It has also been shown[24,25] that C—H---O_{2c} bonding tends to "lock" the DMMP in whatever rotational orientation is selected initially. Thus the relaxed structure may represent only a local, and not a global, energy minimum. In the present work, initial configurations in which the DMMP was rotated by 90 or 180° about the P=O bond, relative to that shown in Figure 2b, were considered; although, only the structure shown was relaxed

all the way to convergence. This geometry appears to be the most stable, but the differences among the relaxed energies are very small (<2 kcal/mol). More importantly, the unusual relaxed structure described below was seen for all three starting configurations. The initial structure in Figure 2b shows the Ti---OP bond at an angle with respect to the surface normal. An initial structure with the Ti---OP bond along the surface normal relaxed into the configuration shown at an early stage in the optimization.

Relaxation (Figure 2c) leads to a breaking of the long Ti_{5c}—O_{2c} bond at the adsorption site, with the terminal O atom then

forming a Ti=O bond with its remaining neighbor. This interpretation is based on the Ti=O distance of 1.634 Å, which is much less than the computed bulk Ti—O distance of 1.967 Å (1.936 Å) parallel (perpendicular) to the [001] axis. The Ti atoms at the Ti=O and DMMP sites relax away from each other in the [100] direction by about −0.66 and +0.36 Å, respectively, relative to the positions on the bare relaxed surface. The O_{2c} atoms bonded to these Ti sites also displace along [100] by about 0.36 Å away from the adsorption site. The Ti in the Ti=O and the remaining O_{2c} to which it is bonded also displace outwardly along the surface normal by about 0.25 and 0.18 Å, respectively. Most of these displacements can be seen qualitatively in Figure 2c. Other atoms exhibit smaller displacements (generally <0.05 Å) in all directions, including [010]. Due to the large displacements in the vicinity of the adsorption site the (4 × 4) supercell may not be sufficiently large to permit complete relaxation, and the ΔE_{ads} value given below must therefore be considered a lower-limit estimate of the low-coverage adsorption energy. Similar considerations affect ΔE_{ads} for the dissociative adsorption of H_2O (see Section 3.2).

The formation of a titanyl Ti=O site is an unusual and unanticipated result. Previously such species (with a bond length of 1.62 Å) were proposed[47] to form on the rutile (011)-(2 × 1) surface. However, recent work[48] has found that other structures, not involving Ti=O, are more stable for that surface. The (0001) surfaces of oxides with the M_2O_3 corundum structure (M ≡ V, Cr, Fe) have been shown both experimentally and theoretically (ref 49 and works cited) to form $M=O$ sites. However, to the best of our knowledge there are no prior reports of Ti=O formation in response to adsorption on a TiO_2 surface. Many other computational studies[36−39,46,50,51] of reactive species adsorbing on anatase (001) have also observed the breaking of a Ti_{5c}—O_{2c} bond. However, the reagents involved (H_2O, CH_3OH, etc.) are all able to release an H atom, which reacts with the singly coordinated O to form a Ti—OH site instead of a Ti=O. The subject of H_2O adsorption is discussed further in Section 3.2. The Ti---O=P bond is characterized by Ti---O and O=P lengths of 1.962 and 1.500 Å respectively and an angle of 163°. The P=O distance is 0.041 Å longer than that computed for the free molecule. After BSSE correction a DFT adsorption energy of ΔE_{ads} = −42.5 kcal/mol was found. The correction, ΔE(BSSE) = 6.6 kcal/mol, was obtained from previous[24,25] 2-DPS calculations for molecular adsorption of DMMP on anatase (101) and (100) surfaces using the same methods and basis sets as those employed here.

Another issue, which relates to the experimental detection of Ti=O (see Section 3.4 below), is whether it persists after removal of adsorbed DMMP. It was found that, with DMMP removed, the long Ti_{5c}—O bond does not reform but instead the Ti=O remains intact with some additional relaxation, consisting of a small (<0.2 Å) displacement inward along the surface normal and toward the vacant adsorption site. The resulting energy is 5.0 kcal/mol lower than that of the relaxed (1 × 1) surface, which represents the exothermic formation energy of the Ti=O. Subtracting this from ΔE_{ads} gives an estimate of −37.5 kcal/mol for the Ti---O=P bond energy, which can be compared with values of −21.0 and −19.1 kcal/mol respectively for molecular adsorption on the (100) and (101) anatase surfaces.[24,25] This trend parallels that in surface energy[35,50] (σ = 0.90, 0.53, and 0.44 J/m^2 respectively for (001), (100), and (101)), which indicates that the Ti---O=P bond energy decreases with increasing surface stability (i.e., decreasing σ). The rutile (110) surface also fits this pattern, with ΔE_{ads} = −17.6 kcal/mol and σ = 0.31 J/m^2.

3.2. Test Calculations. Several tests were done to validate the procedures described above and to demonstrate that the Ti=O is not an artifact of the calculation. Those involving different initial configurations for adsorbed DMMP have been described in the previous section. Geometry optimizations for adsorbed DMMP using RHF vs DFT, as described in Section 2, were compared, and the differences in atomic displacements were negligibly small (~5% or less). The BSSE-corrected ΔE_{ads} for the relaxed structures (both obtained in single-point DFT calculations with all-electron basis sets) were −42.5 vs −40.3 kcal/mol. A similar comparison for the bare (1 × 1) surface has been discussed already (cf. Table 1). In another test, RHF geometry optimization was done for a different 2-DPS model, one with eight O—Ti—O trilayers, a (3 × 3) supercell and DMMP placed symmetrically on both surfaces so as to maintain the center of inversion of the supercell. All atoms were unconstrained in the relaxation, and the same structure as that described above, including the Ti=O site, was obtained.

Finally, the adsorption of H_2O was considered. Several DFT plane-wave/pseudopotential calculations[38,39,46,50,51] have found that, at low coverage, H_2O dissociates spontaneously on the anatase (001) surface. This is accompanied by the breaking of a Ti_{5c}—O_{2c} bond and the formation of an H-bonded pair of Ti_{5c}—OH sites with ΔE_{ads} in the range of −32 to −39 kcal/mol. ΔE_{ads} decreases significantly with increasing coverage,[46,50,51] which may indicate a repulsive interaction due to the large atomic displacements in the vicinity of an adsorption site. This calculation was repeated, using the same model and methods as employed for DMMP, beginning with H_2O adsorbed molecularly at a Ti_{5c} site on the relaxed (1 × 1) surface (Figure 3a). The H_2O was adsorbed via a Ti---O bond with the 2-fold axis normal to the surface and with the plane of the molecule lying in the (010) plane. The coverage was one H_2O per (4 × 4) supercell, i.e., one H_2O per 16 surface Ti_{5c} sites, but one per 4 Ti_{5c} sites on the [100] axis along which most of the relaxation occurs. Early in the relaxation (within 6 optimization steps) the long Ti_{5c}—O_{2c} bond broke, and a Ti=O bond formed with a minimum interatomic distance of 1.650 Å (Figure 3b). Continued relaxation led to the transfer of an H to form a Ti—OH, resulting in the same H-bonded pair of Ti—OH sites as previously reported (Figure 3c). Thus the Ti=O site is found to be an intermediate in the dissociative adsorption of H_2O.

3.3. Adsorption on the (4 × 1) Surface. The atomically clean anatase (001) surface is known from experiment to exhibit a (4 × 1) reconstruction.[52−54] Ab initio modeling[45] shows that this is driven by the large reduction in surface energy that follows from the decrease in the tensile stress intrinsic to the (1 × 1) surface. Figure 4a shows the ad-molecule (ADM) structure[45] in which one of four O_{2c} rows in the [010] direction (cf. Figure 2) is replaced with TiO_3 units to form three O_{2c} and one Ti_{4c} site per (4 × 1) unit cell. The increase in energy due to the addition of coordinatively unsaturated surface atoms is more than offset by the relaxation of the remaining Ti_{5c}—O_{2c} bonds to "normal" lengths. As expected, a Ti_{4c} ridge site is found experimentally[55,56] and computationally[37,46] to be more reactive than a Ti_{5c} terrace site. In particular, spontaneous dissociation of H_2O to form two Ti—OH groups has been reported[37,55] to occur at Ti_{4c} ridge sites but not at Ti_{5c} terrace sites. It is noted that formation of the (4 × 1) reconstruction requires annealing at high temperature (~1050 K, ref 52) and might not occur at the lower temperatures typically used in studies employing HSA powders. Hence, the results described above for the (1 × 1) surface remain relevant.
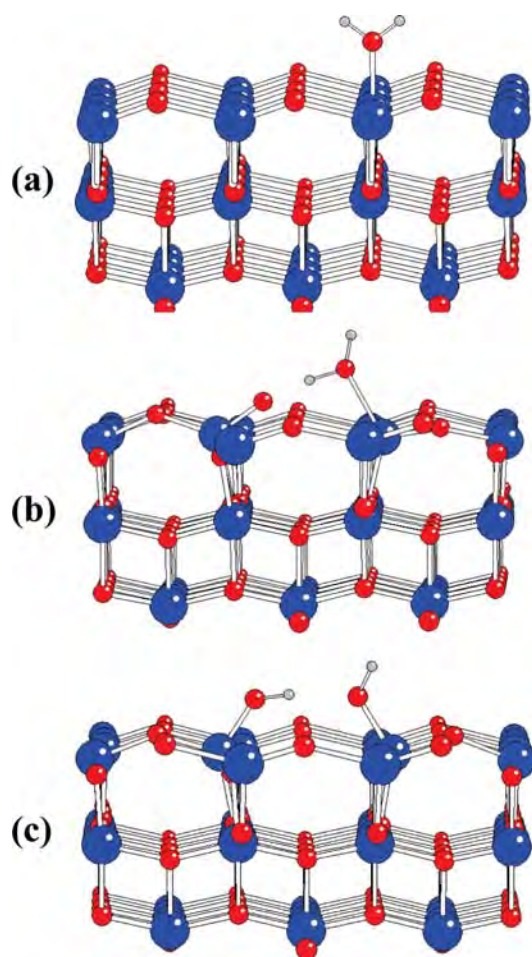
Figure 3. Stages in the dissociative adsorption of H_2O. (a) The initial molecularly adsorbed state. (b) After 9 optimization steps, showing a Ti=O group H-bonded to molecular H_2O. (c) After an additional 29 steps, showing a pair of H-bond Ti—OH sites. Transfer of the H atom occurs at optimization step number 24.
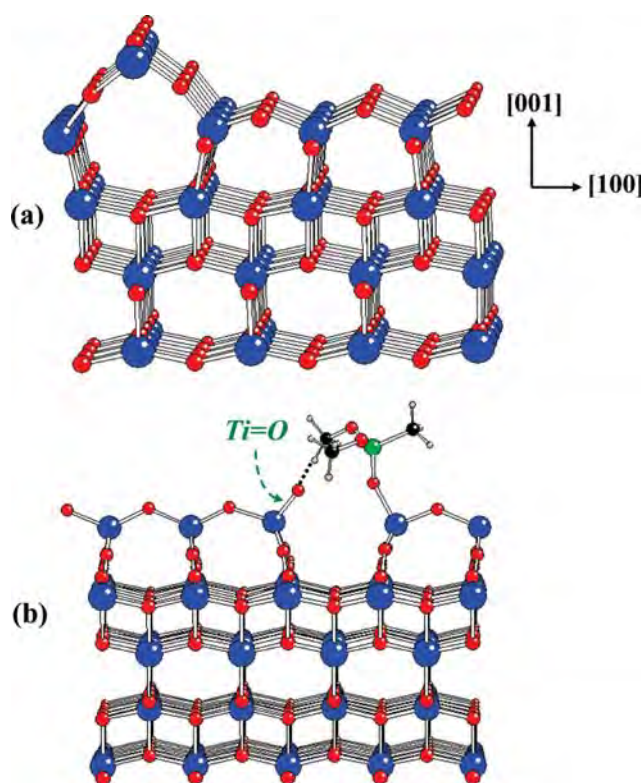

Figure 4. Like Figure 2 but for the (001)-(4 × 1) surface. (a) Relaxed, bare (4 × 1) surface viewed along [010] direction, i.e., parallel to the ridge. (b) Same surface after adsorption of DMMP and relaxation, viewed along the [100] direction (i.e., perpendicular to the ridge). The dashed line in (b) shows a possible H-bond.

Following previous studies[37,46] of adsorption on the (001)-(4 × 1) surface, the model used here is asymmetric, with reconstruction on only one slab surface and the other held fixed with atoms in the ideal bulk-lattice positions (cf. Section 2).

The surface bond lengths obtained for the bare (4 × 1) surface agreed well with, but were about 1% smaller than, those previously reported.[45] A small fraction of this difference is due to the slightly smaller bulk [100] lattice constant (a = 3.781 vs 3.786 Å) used in the present work. The Ti_{4c}—O_{2c} bond lengths of 1.965 and 1.974 Å are close to the computed bulk Ti—O bond lengths of 1.936 and 1.967 Å. Figure 4b shows the relaxed structure for adsorbed DMMP, which, similarly to the (1 × 1) result, exhibits the breaking of a T_{4c}—O_{2c}—Ti_{4c} bridge and the formation of a Ti=O site with a bond length of 1.637 Å. Since the Ti=O Ti is then 5-fold coordinated, the stabilization of this structure is thought to result from the decrease in the degree of coordinative unsaturation. A BSSE-corrected ΔE_{ads} of −58.4 kcal/mol was obtained. In agreement with previous work,[37] ΔE_{ads} at a Ti_{4c} ridge site is significantly higher than at a (1 × 1) Ti_{5c} site. As in the case of the (1 × 1) surface, relaxation after removal of adsorbed DMMP led to the continued presence of the Ti=O

site. However, the energy in this case was only slightly lower, by 1.3 kcal/mol, than that of the bare relaxed (4 × 1) surface.

3.4. Experimental Observables. Techniques that may be suitable for detecting Ti=O are vibrational spectroscopy, ultraviolet photoemission spectroscopy (UPS), and scanning tunneling spectroscopy (STS). Although the ν(Ti=O) stretching-mode frequency has not been obtained in the present work, experiment shows that the corresponding modes for V=O, Cr=O, and Fe=O on the (0001) surfaces of M_2O_3 oxides all occur in the 990−1040 cm^{-1} (123−129 meV) range.[49] Observation of ν(Ti=O) in the presence of adsorbed DMMP would be complicated by the strong DMMP absorption band[57,58] near 1032 cm^{-1}. However, the results discussed above show that the Ti=O persists after removal of the DMMP. Hence, ν-(Ti=O) might be observable if DMMP can be desorbed under conditions that do not also eliminate the Ti=O. Experiment[7] shows that molecular desorption of DMMP, accompanied by some decomposition, occurs at about 440 K for rutile (110). However, ΔE_{ads} for DMMP on this surface is only −17.6 kcal/mol (ref 25), which is significantly lower than on the anatase (001). Thus, it remains to be seen whether DMMP can be thermally desorbed from the (001) surface without removing the Ti=O. Another potential difficulty in vibrational spectroscopy is the presence of the anatase transverse-optic (TO) phonon[59] at 838 cm^{-1}. The width and intensity of the TO phonon peak might partially obscure ν(Ti=O) in an infrared reflection−absorption or a high-resolution electron energy loss experiment.
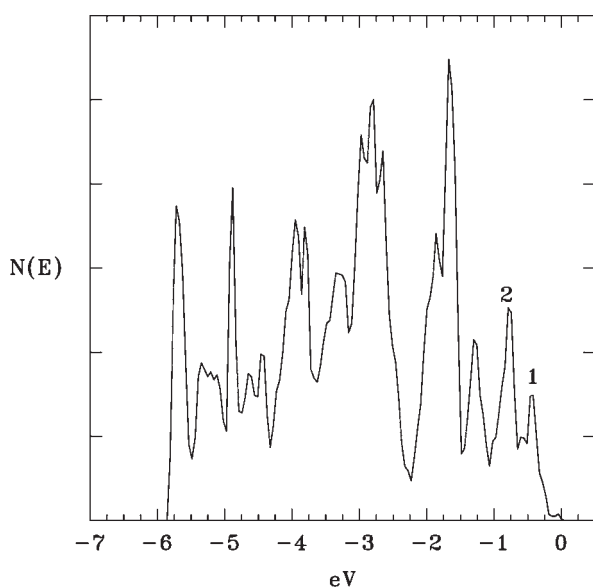
Figure 5. Total DOS, for all atoms in the 2-DPS supercell, for the (1×1) surface after removal of adsorbed DMMP and subsequent relaxation. The labeled features receive contributions from the Ti═O bond. The zero of energy is at the bulk valence band maximum.

In the model originally proposed[47] for the rutile (011)-(2×1) surface, Ti═O produces a narrow feature in the density of states, not seen for other stoichiometric TiO_2 surfaces, at 1 eV below the VBM. Similar features are seen in the computed (1×1) density of states (DOS) shown in Figure 5 and have been assigned using the partial DOS for individual atoms. These results were obtained after relaxing the surface following removal of adsorbed DMMP, and the Monkhorst-Pack grid was increased to (4×4) for computation of the DOS. The main contribution from the Ti═O bond is in Peak 1, at ~0.45 eV below the bulk VBM, which falls on top of structure derived from other atoms. There is also some Ti═O contribution to Peak 2, but a large part of the density here is derived from surface O_{2c} atoms. A similar Peak 1, although much less pronounced, is found for the (4×1) surface after removal of DMMP (not shown). Here again the features of interest may be obscured in UPS or STS by structure due to adsorbed DMMP. However, the same remarks about the removal of DMMP, made in connection with ν(Ti═O), also apply here.

No empty states localized on the Ti═O were found in the DOS at or below the conduction band minimum (CBM, not shown). Hence, Ti═O might not easily be detected using electron energy-loss spectroscopy (ELS) as a probe of electronic excitations associated with this site. Such empty states are seen at about 1.5 to 2.5 eV above the CBM, and ELS transitions involving the Ti═O might be obscured by stronger interband excitations.

4. CONCLUSIONS

The molecular adsorption of DMMP on the OH-free TiO_2 (001)-(1×1) and -(4×1) surfaces was modeled using ab initio calculations. The adsorption is exothermic, with ΔE_{ads} of -42.5 and -58.4 kcal/mol, respectively. Relaxation leads to the breaking of the long Ti_{5c}—O_{2c} bond in the case of the (1×1) surface, or a Ti_{4c}—O_{2c} bond in the case of the (4×1), and the formation of a Ti═O bond at a neighboring Ti site. To the best of our

knowledge, Ti═O formation in response to adsorption has not previously been reported for any TiO_2 surface. Results presented here for H_2O adsorption on the (1×1) surface suggest that a Ti═O intermediate is important in dissociative chemisorption, and consequent Ti—OH formation, for species with one or more labile H atoms. It is speculated that other adsorbates (e.g., acetone), which might form a dative bond to a Ti_{4c} or Ti_{5c} without decomposing to form Ti—OH, could also produce a stable Ti═O site. Also, a well-chosen alternative to DMMP would not interfere with spectroscopic detection of the Ti═O, thus making desorption unnecessary. However, a "strong" dative bond may be required for Ti═O formation to occur. For example, a recent study[60] of thiophene adsorption on anatase (001)-(1×1) via a Ti_{5c}--S dative bond, with a ΔE_{ads} of only -5.4 kcal/mol, shows no breaking of the Ti_{5c}—O_{2c}—Ti_{5c} bridge and hence no Ti═O formation. The implication is that a sufficiently strong adsorption bond to the Ti_{5c} weakens the long Ti_{5c}—O_{2c} bond enough to overcome the barrier to breaking this bond and forming the Ti═O. The existence of such a barrier would account for the fact that Ti═O does not form spontaneously during relaxation of the bare surface.

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